

# Near-equilibrium polymorphic phase transformations in praseodymium under dynamic compression

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The authors report the first experimental observation of sequential, multiple polymorphic phase transformations occurring in praseodymium dynamically compressed using a ramp wave. The experiments also display the signatures of reverse transformations occurring upon pressure release and reveal the presence of small hysteresis loops. The results are in very good agreement with equilibrium hydrodynamic calculations performed using a thermodynamically consistent, multiphase equation of state for praseodymium, suggesting a near-equilibrium transformation behavior. © 2007 American Institute of Physics. [DOI: 10.1063/1.2732831]

The transition metals form an interesting class of materials with complex phase diagrams strongly correlated to the evolution of their electronic structure under applied pressure. Following the enhancement in the *d*-band occupancy, which at lower pressures results in slight atomic rearrangements in high symmetry structures with negligible density changes, several lanthanides also undergo phase transformations to lower symmetry structures marked by significant volume collapses and a delocalization of the 4*f* electrons.<sup>1–3</sup> Praseodymium (Pr) is a representative example for this type of behavior. Comprehensive theoretical studies up to several megabars have created a rich basis for understanding both its thermodynamic and electronic properties at elevated pressures.<sup>4</sup> A wealth of static high pressure studies has engaged a range of techniques to map the material behavior under compression. While early experimental studies focused on static pressure conditions<sup>5–9</sup> or nearly instantaneous shock loading conditions,<sup>10</sup> recent developments have enabled explorations on intermediate time scales.<sup>11–13</sup>

We carried out comprehensive dynamic compression experiments on high-purity (99.9%) polycrystalline praseodymium. Disk shaped samples, 6 mm in diameter and with thicknesses of 0.4 and 0.52 mm, were prepared, metrologized, and encapsulated between aluminum (Al) panels and a transparent window, under controlled argon (Ar) atmosphere in order to preclude oxidation. Four identical panels, as shown in Fig. 1, were arranged symmetrically around a central cathode to form the anode of the Z accelerator. The controlled discharge of a large capacitor bank generates a magnetically driven pressure wave with an  $\approx 35$  GPa amplitude and a rise time of  $\sim 400$  ns, followed by gradual release at the left boundary of the panels, Fig. 1. The loading pressure was carefully designed to avoid field penetration before the end of the experiment, or the development of shocks in the sample, and was monitored on each panel with a reference probe. Variations of 2%–3% were registered in the maximum pressure between panels and were ascribed to possible local differences in the corresponding panel/cathode spacing. We measured the velocity of the sample/window interface during the experiment using interferometric techniques [velocity interferometer system for any reflector (VISAR)].<sup>14</sup> Four interferometer probes were pointed at the

center of each sample, with two or more different sensitivities in order to eliminate fringe loss uncertainties. Three types of windows were used in the experiments: [100] single crystal lithium fluoride LiF, polymethyl metacrylate (PMMA) and *z*-cut sapphire Al<sub>2</sub>O<sub>3</sub>. Their optical properties in the pressure-temperature regime accessed in these experiments have been well studied and are summarized in Ref. 15.

As a result of the rapidly applied pressure, the samples are compressed along a quasi-isentropic thermodynamic path that intercepts several Pr phase boundaries during both the compressive and subsequent release regimes—see Fig. 2 and the discussion below. As noted in Ref. 12, the dynamic impedance of the window plays an important role in the evolution of the phase transformations inside the sample. This effect is clearly illustrated by the present experiments which, as mentioned above, have been carried out with three types of windows: the “stiff” sapphire window produces a significant pressure enhancement at the interface, “soft” PMMA leads to a pressure drop at the interface, while LiF single

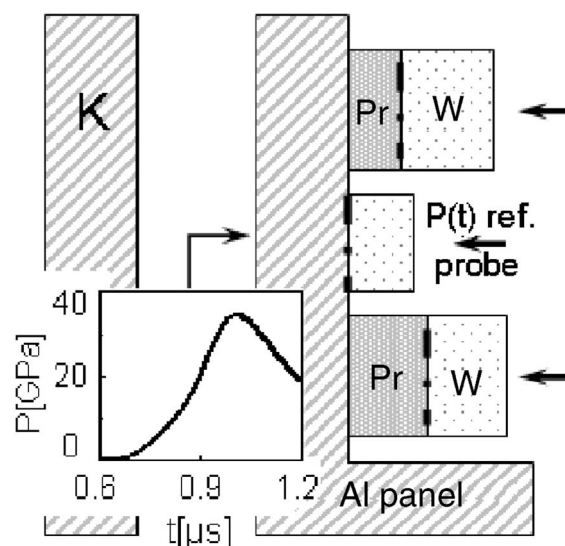


FIG. 1. Schematic cross section through one of the four experimental cells (panels) displayed in a square geometry around the cathode of the Z accelerator. Pr sample is encapsulated between the Al panel (1 mm thick, dashed) and the transparent window (W). A rapidly varying magnetic field in the 3 mm panel/cathode (K) gap generates the compression wave—see  $P(t)$  inset;  $P(t)$  is measured *in situ* by the reference probe. Drawing not to scale.

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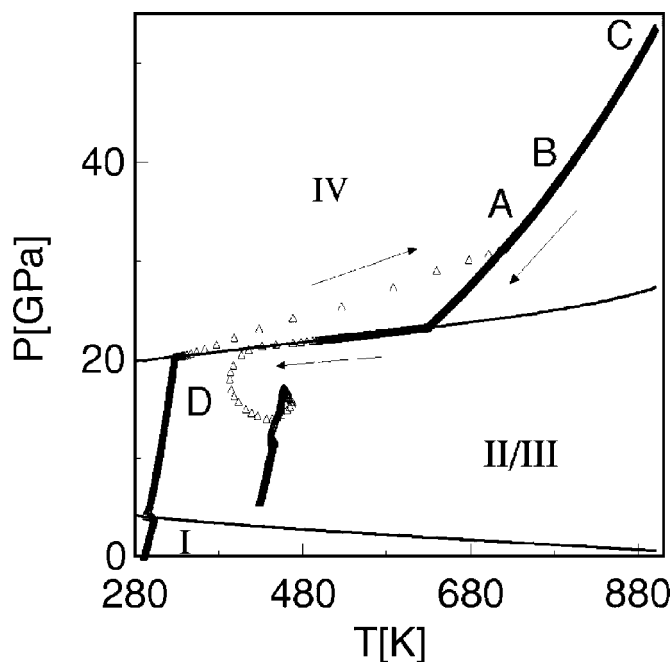


FIG. 2. Model Pr phase diagram and characteristic thermodynamic path (symbols) describing the evolution of the sample. Compression and release paths indicated by arrows. A, B, and C mark the maximum pressures achieved with PMMA, LiF, and  $\text{Al}_2\text{O}_3$  windows, respectively. D marks the maximum pressure attained at the Pr/PAMMA interface—below transformation conditions.

crystal, relatively closely dynamically matched to Pr, provides a nearly *in situ* response. The general differences between the experimental traces shown in Fig. 3 are rather obvious, although they all display the characteristic changes in velocity slope (acceleration) associated with the occurrence of phase transitions.<sup>12</sup>

The detailed dynamic response of Pr under compression can be better understood by comparing the measured inter-

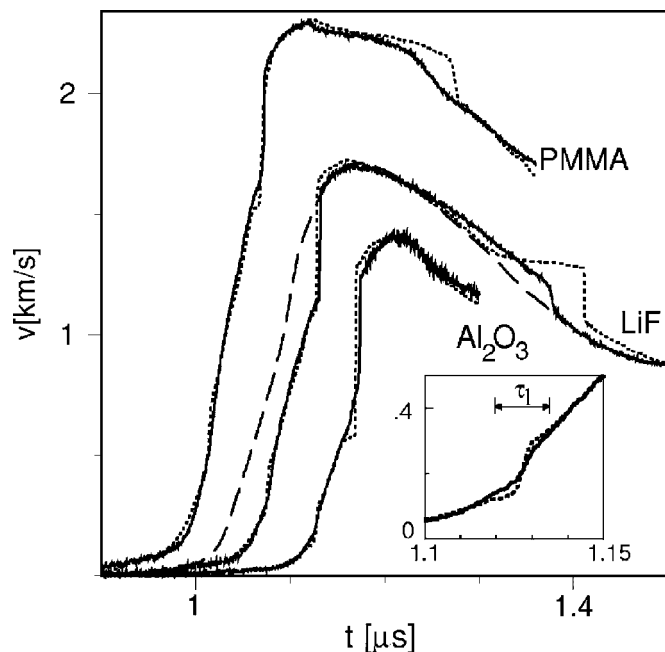


FIG. 3. VISAR traces for the Pr sample with PMMA ( $t \sim 50$  ns), LiF, and  $\text{Al}_2\text{O}_3$  ( $t \sim 50$  ns) windows (solid lines) corresponding hydrodynamic simulations using three phase equation of state (EOS) for Pr (dotted lines), and using single phase EOS (dashed line). The inset details the region of the Pr/ $\text{Al}_2\text{O}_3$  velocity curve where the first phase transformation occurs.

face velocity  $v(t)$  to one-dimensional hydrodynamic simulations mimicking the experimental setup. We performed such calculations using a multiphase equation of state for Pr derived from a thermodynamically consistent free energy model,<sup>16</sup> Mie-Grüneisen equations of state for the Al panels and windows,<sup>17</sup> and the applied pressure history measured by the reference probes. At ambient conditions Pr assumes a *dhcp* structure with initial density  $\rho_0 = 6.78 \text{ g/cm}^3$ , while under pressure it undergoes a sequence of phase transformations that is specific to the lanthanide series  $\text{PrI} \rightarrow \text{PrII fcc} \rightarrow \text{PrIII distorted fcc} \rightarrow \text{PrIV orthorhombic } \alpha\text{-U}$ . Several comprehensive studies<sup>1,6,8</sup> indicate that the differences between the PrII (fcc) and PrIII (*dfcc*) phases are minimal, and therefore we used a single representation for them in the model. The PrIII  $\rightarrow$  PrIV transition is marked by a large volume collapse which has been explained in terms of *f* electron delocalization. Model phase boundaries shown in Fig. 2 are in very good agreement with prior experimental determinations.<sup>7,8</sup> The principal Hugoniot<sup>10</sup> and the isotherms measured in Ref. 8 are also reproduced with better than 2% accuracy.

Our calculations indicate that in the present experiments Pr should undergo two polymorphic phase transformations, at  $\sim 4$  and  $\sim 20$  GPa, which are marked by slope discontinuities of the interface velocity, e.g., at  $\sim .12$  and  $\sim .56 \text{ km/s}$  respectively, for the case of a sapphire window, Fig. 3. The experimental  $v(t)$  traces clearly exhibit such features, but at slightly larger pressures. An approximately 5%–10% over-compression, as compared with simulations, is consistently observed in the experiments for all samples and at both  $[\text{PrI} \rightarrow \text{PrII(III)}]$  and  $[\text{PrII(III)} \rightarrow \text{PrIV}]$  phase transformations. We estimate that the PrI  $\rightarrow$  PrII transition occurs in our experiments on time scales  $\tau_1 \sim 15 \text{ ns}$ . The  $\tau_1$  value was determined as the time between the onset of the discontinuity in the interface acceleration and the subsequent merging of the experimental and simulated  $v(t)$  traces, marking the completion of the transformation—see Fig. 3 inset. Similarly, we estimate that fcc Pr transforms to the  $\alpha\text{U}$  phase on a  $\tau_2 \sim 10 \text{ ns}$  time scale, see Fig. 3, measured again from the  $v(t)$  change in slope (i.e., onset of transition) to the discontinuity of the interface velocity signaling the achievement of a fully transformed state. The experimental data show no evidence for significant changes in material properties between 4.5 and 22 GPa, consistent with the initial assessment regarding the similarity of the PrII and PrIII phases. The  $\text{Al}_2\text{O}_3$  and LiF windows generate the highest pressures in the Pr sample ( $\sim 55$  and  $40 \text{ GPa}$ , respectively), causing the entire sample to eventually undergo the transformation to the  $\alpha\text{-U}$  phase. No evidence for additional phase transformations following the formation of PrIV is seen up to 55 GPa and  $\sim 900 \text{ K}$ , the maximum pressures, and temperatures achieved in our experiments.

We note that, as indicated by the sample bulk thermodynamic paths in Fig. 2, both the PMMA and LiF windows allow the occurrence of the reverse  $\alpha\text{-U-dfcc}$  transformation. In the case of the LiF window, the velocity jump marks the completion of the transition to PrIV in the compressive regime, see Fig. 3. Upon releasing the pressure a short plateau followed by a sudden drop in velocity is observed at  $\sim 1.35 \mu\text{s}$ , signaling the onset of the reverse transition at the interface. By comparing the relative positions of the velocity plateau in the experiment and the simulation, we estimate that the metastable regime extends below the equilibrium phase boundary.

rium phase line by approximately 1 GPa, comparable with the amount of overcompression registered upon crossing the phase boundary in the opposite direction.

The PMMA window is much softer than the Pr and it produces a large pressure drop in the vicinity of the interface. Consequently, the material at and near the monitored surface does not actually transform to PrIV, and the signature observed is that of the advancing transformation front in the bulk of the sample.<sup>12</sup> The nearly flat  $v(t)$  response between 1.12 and 1.22  $\mu\text{s}$  in Fig. 3 is directly related to the inverse transformation occurring in the bulk of the Pr sample. The reverse transformation most likely completes around 1.28  $\mu\text{s}$ , as suggested by the merging of the experimental and equilibrium simulation curves.

Finally, a comparison between the experimental data and hydrodynamic simulations using only a simple, single phase Mie-Grüneisen model for Pr derived from the principal Hugoniot measurements, see Fig. 3, illustrates the sensitivity of the ramp compression technique and its ability to reveal subtle phase transformations. It is worth noting that practically no volume change is detected in static compression experiments for the PrI $\rightarrow$ PrII transition, the transformation being diagnosed solely on the changes in the diffraction spectrum.<sup>9</sup> Shock Hugoniot measurements have only been able to detect the PrIII $\rightarrow$ PrIV transition.

In conclusion we report the first observation of sequential, multiple polymorphic phase transformations occurring upon quasi-isentropic compression and release of pure praseodymium. By employing different windows we probe the effect of boundary conditions on the phase transformation paths and experimental signatures and access three representative regimes. The experimental features on both compression and release are very well reproduced for all windows by a multiphase, thermodynamically consistent equation of state for Pr. The excellent agreement between experimental data and hydrodynamic simulations suggests that the phase transformations proceed along near-equilibrium paths. We observe small hysteresis loops and estimate the extent of the dynamically explored metastability region around the equilibrium phase boundaries to be 5%–

10% of the transition pressure. We evaluate transformation characteristic time scales of order of 10 ns.

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